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MINERAL COMMODITY REPORT

—— CALCIUM CHLORIDE ——

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By

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Part I compiled from
the U.S. Bureau of Mines publication,
Minerals Yearbooks, 1980—82.

CALIFORNIA DEPARTMENT OF CONSERVATION

DIVISION OF MINES AND GEOLOGY

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INTRODUCTION

This report on the availability and demand for calcium chloride in the United States, the world, and California, is one of a series of Mineral Commodity Reports prepared by the Department of Conservation's Division of Mines and Geology (DMG) to describe mineral commodities of significant importance to California and the nation.

This report was compiled by Hasmukhrai H. Majmundar of the DMG geologic staff. Part I of the report consists of United States and world-wide mineral-statistic information and analysis. Part II discusses production of the commodity in California. The U.S. Bureau of Mines presents the earliest Government estimates of non-fuel mineral-industry data, including world resources data provided by the U.S. Geological Survey. Unlike the other commodity reports in this series which use the current U.S. Bureau of Mines "Mineral Commodity Summaries" as the basis of Part I, this report on calcium chloride is a compilation of entries from the calcium and calcium compounds sections of the U.S. Bureau of Mines "Mineral Yearbooks" from 1978-1982. The U.S. Bureau of Mines does not include a section in calcium chloride in the annual "Mineral Commodity Summaries."

In 1982, the United States produced 854,000 short tons of calcium chloride, imported 61,000 short tons for consumption, exported 55,000 short tons, and had an apparent consumption of 860,000 short tons. The imports were from Canada (37 percent) and Mexico (63 percent). Although the production statistics for all the facilities are confidential, the total production in 1983 is estimated to be 890,000 short tons of combined natural and synthetic calcium chloride.

Calcium chloride is utilized mostly because of its capacity for absorbing water and the tendency of its solutions to freeze at low temperatures. In the United States, about 35 percent of the calcium chloride produced is used for deicing the roads, 20 percent each for dust control and coal and bulk material thawing, 12 percent for oil and gas drilling, 5 percent for concrete setting, and 4 percent each for tire ballasting and miscellaneous uses. Markets for calcium chloride in California have not grown as fast as those of the rest of the United States because of mild winter weathers.

About two-thirds of the calcium chloride produced in the United States is obtained from natural terrestrial brines pumped either from Paleozoic formations or from the late Quaternary deposits. The remaining one-third is produced synthetically. Calcium chloride is a highly hygroscopic salt that always occurs in solution. It is so hygroscopic that even solutions of calcium chloride are hygroscopic. Calcium chloride is present in the saline minerals with complex chemistry, occurring in tachydrite ($CaCl_2.2MgCl_2.12H_2O$) and as an impurity in carnallite ($KCl.MgCl_2.6H_2O$).

For further information, please call (916) 445-5716, the DMG centralized information number.

PART I: UNITED STATES AND WORLDWIDE

1. UNITED STATES PRODUCTION AND USE

Calcium chlorite: Total output in California decreased 29% in 1982 compared with that of 1981. Total output in Michigan also decreased 12% in 1982 compared with that of 1981. Total 1982 domestic production of natural calcium chloride decreased 13% compared with 1981 production. Total 1982 domestic production of synthetic calcium chloride, however, increased 12% compared with the 1981 level. Thus, the total value of domestic calcium chloride increased to $92,762,000 in 1982 from that of $88,778,000 in 1981.

Calcium chloride was used for road and pavement deicing, 35%; dust control and road base stabilization, 20%; and for industrial uses, including coal and bulk material thawing, 20%; oil and gas drilling, 12%; concrete-set acceleration, 5%; tire balasting, 4%; miscellaneous uses, 4%. The most rapidly growing end use was in well completion fluids in oil and gas recovery. The principal domestic use of calcium chloride was to melt snow and ice from roads, streets, bridges, and pavements. Calcium chloride is more effective at lower temperatures than rock salt and is used mainly in the northern and eastern states. Because of its considerably higher prices, it is used by mixing it with rock salt for maximum economy and effectiveness.

Calcium chloride is usually sold either as solid flake or pellet, averaging about 75% $CaCl_2$, or as a liquid concentrate, averaging 40% $CaCl_2$.

2. SALIENT STATISTICS -- UNITED STATES

Calcium chloride (Data in thousand short tons, unless noted):

Production:	1978	1979	1980	1981	1982
Natural	773	720	581	705	617e
Synthetic	258	261	230	212	237e
Total	1,031	981	811	917	854
Imports for consumption:	43	58	46	87	61
Exports:	NA	NA	49	33	55
Apparent consumption:	--	--	808	971	860
Price (average annual): per ton, f.o.b. warehouse basis[1]					
Flake (75%)	$79.42	$86.06	$111.90	120.57	$120.57
Liquid (40%)	$31.91	$25.89	$33.22	$34.64	$34.64
Stocks: yearend	NA	NA	NA	NA	NA
Employment:	NA	NA	NA	NA	NA
Net import reliance[2] as a percent of apparent consumption	NA	NA	NA	NA	NA

e Estimated. NA = Not available.
1 Average value for combined natural and synthetic products.
2 Defined as imports-exports + adjustments for Government and industry stock changes.

3. RECYCLING

None

4. IMPORT SOURCES (1978-82)

1978 and 1979, Canada 100%; 1980, Canada 60.5% and Mexico 39.5%; 1981, Canada 33% and Mexico 67%; 1982, Canada 37% and Mexico 63%.

5. TARIFF

Data not available.

6. DEPLETION ALLOWANCE

Data not available.

7. GOVERNMENT STOCKPILE

None.

8. EVENTS, TRENDS, AND ISSUES

In 1982-83, natural calcium chloride was produced by five companies in California and three companies in Michigan. Synthetic calcium chloride was manufactured by four companies in their five manufacturing plants, two in Louisiana, one in New York, and two in Washington State.

Exports of calcium chloride to 52 countries in 1982 increased 68% in quantity, but decreased 15% in value compared with 1981 exports. Eleven countries received more than 500 tons of calcium chloride from the United States. The average annual price of calcium chloride per ton f.o.b. plant warehouse remained the same in 1981 and 1982. Imports of calcium chloride were mainly from Mexico and Canada.

Allied Chemical of Morristown, New Jersey built a new plant for the production of 38% liquid synthetic calcium chloride at its Baton Rouge, Louisiana complex in 1981. In the same year, Texas United Chemical Corporation started producing synthetic calcium chloride from purchased hydrochloric acid and limestone at its plant near Lake Charles, Louisiana.

Velsicol Chemical Corporation, a subsidiary of Northwest Industries, was forced to close its St. Louis, Michigan chemical plant in September 1978 because of environmental pollution of polybrominated biphenyls. At least 60,000 tons per year of 78 percent-equivalent $CaCl_2$ was lost to the marketplace, and disrupted a market that had price increases totaling over 14% for that year.

9. WORLD MINE PRODUCTION AND RESERVE BASE

Data on world mine production in the "Minerals Yearbook" chapters are incomplete.

10. WORLD RESOURCES

Domestic calcium chloride resources are inexhaustible. Other North American resources in Mexico and Canada are also inexhaustible. Other countries have very limited resources of calcium chloride.

11. SUBSTITUTES

Calcium chloride may be substituted by rock salt in deicing roads, but the latter is not as effective. Rock salt can not be substituted in dust control and road base stabilization, coal and bulk material thawing, and for concrete-set-acceleration.

PART II: CALIFORNIA

12. CALIFORNIA GEOLOGICAL OCCURRENCES

Approximately two-thirds of the calcium chloride produced in the United States is obtained from natural brines; the other one-third is by synthetic production (Smith, 1966). In the United States, Michigan produces about 95%, California about 4%, and West Virginia about 1% of the calcium chloride (Babcock, 1964). To produce calcium chloride in California, brine is pumped from the late Quaternary deposits in Bristol and Cadiz Lakes, whereas in Michigan and West Virginia it is pumped from the Palaeozoic formations. Synthetic calcium chloride is manufactured as a byproduct of the Solvay sodium carbonate process in New York, Ohio, and Washington States.

Calcium chloride is a white, soluble, hygroscopic salt that most commonly occurs in solution. It is hygroscopic to such an extent that even the solutions of calcium chloride are hygroscopic. The anhydrous calcium chloride easily absorbs more than its weight of water in 24 hours. The only natural sources of calcium chloride of commercial importance are the chloride type of terrestrial brines in which calcium ions are approximately equal to the sodium ions. In such brines, magnesium is in minor amounts, but sulfate and carbonate are very low. Calcium chloride is present in the saline minerals, with complex chemistry, occurring in tachydrite ($CaCl_2.2MgCl_2.12H_2O$) and also as an impurity in carnallite ($KCl.MgCl_2.6H_2O$).

In California, calcium chloride is recovered from the brines of Bristol and Cadiz Lakes in San Bernardino County. These two lakes occupy adjacent basins lying in the east-central part of the Mojave Desert region. The fill beneath the floor of Bristol Lake contains more than a thousand feet of salt and clay sediments (Bassett and others, 1959), but the drilling evidence confirms that the calcium chloride-rich brine is largely confined to the uppermost 32 feet (Gale, 1951). Both of these lakes have a number of salt beds interbedded with clayey sediments common in a playa lithology. The salt producing uppermost beds are considered mineable for over a five-square-mile area in Bristol Lake. The brine, in general, contains calcium and sodium chloride as the main dissolved solids.

Cadiz Lake has similar, but less rich, calcium-chloride brine. It has also similar interbedded salt and clay stratigraphy, and the calcium chloride is higher in the uppermost saline beds.

Bristol and Cadiz Lakes have unusual, high-calcium, chloride-rich brines that must have been formed under unusual geologic conditions. There have been two geologic hypotheses put forward by various geologists for the origin of this unusual chemistry of the two lakes, but neither is satisfactory. Some geologists consider recent volcanism associated with the Amboy or Bagdad crater responsible for this high calcium chloride contents (Gale, 1951). Other geologists hypothesize that the calcium chloride originated as the result of a base-exchange process in which calcium of the clay (mineral) molecules in certain clay beds has been exchanged for a part of the sodium of the sodium brine (Rosenstein and Ludwig, 1954; Ver Planck, 1957).

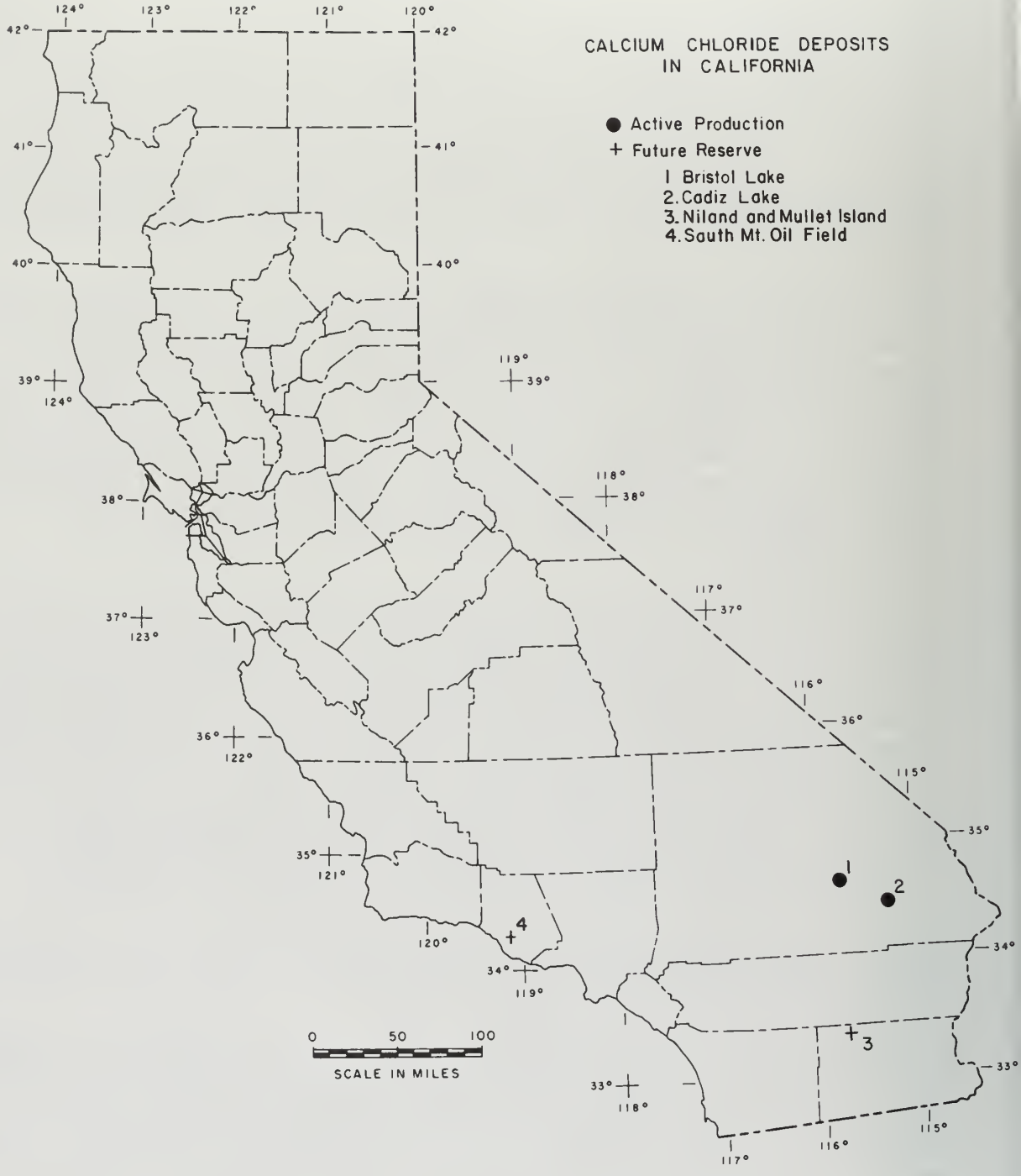

Figure 1. Calcium Chloride Deposits in California.

13. CALIFORNIA LOCALITIES

In California, the calcium chloride brines occur in Bristol and Cadiz Lakes in San Bernardino County; in the oil field brines of Ventura County; in an artesian well on Mullett Island, in brines near Niland, and in brines of certain springs and geothermal wells in Imperial County (Figure 1).

Leslie Salt Company, a subsidiary of Cargill, Inc. of Minnesota, and National Chloride Company of America produce liquid calcium chloride from the brines of Bristol Lake near Amboy. The third company in Amboy, Hill Brothers Chemical Company, buys liquid calcium chloride from Leslie Salt Company and converts it into anhydrous flakes of calcium chloride. Hill Brothers Chemical Company also has a small operation that produces liquid calcium chloride from the brines of Cadiz Lake. Two other companies, Delta Chemical Company and Lee Chemical Company, also produce liquid calcium chloride from the brines of Cadiz Lake. A few years back, Lee Chemical Company bought out Helen M. Tull Company, which was also in the business of producing liquid calcium chloride from the brines of Cadiz Lake.

14. CALIFORNIA PRODUCTION

In California, there are total of five companies producing liquid as well as solid flake calcium chloride from the dry lake brines. These facilities are the Leslie Salt Company, a subsidiary of Cargill, Inc. of Minnesota, National Chloride Company of America, Hill Brothers Chemical Company, Delta Chemcial Company, and Lee Chemical Company. Leslie Salt Company and National Chloride Company of America operate in Bristol Lake near Amboy, in San Bernardino County. Hill Brothers Chemical Company has a plant in Amboy to convert liquid calcium chloride into flakey (solid) calcium chloride. They also have a smaller operation in Cadiz Lake, San Bernardino County. Delta and Lee Chemical Companies operate in Cadiz Lake. A few years back, Lee Chemical Company bought out Helen M. Tull operations in Cadiz Lake. All of these chemical companies manufacture calcium chloride from the brine. The production statistics for all five facilities of California are confidential, but the total is estimated to be 35,000 short tons (in equivalent to 75% calcium chloride) per year.

From Bristol and Cadiz Lakes, the liquid as well as the flakey, anhydrous calcium chloride is sent to most of California, Oregon, Nevada, Utah, Arizona, Wyoming, and Colorado.

15. UTILIZATION AND MARKETS

Calcium chloride is utilized for its capacity to absorb water and for the tendency of its solutions to freeze at low temperatures. In the United States, about 35 percent of the calcium chloride produced is used for deicing road and pavement surfaces, 20% for dust control and road base stabilization, 20% for coal and bulk material thawing, 12% for oil and gas drilling, 5% for inhibiting the loss of moisture in concrete during setting and curing, 4% for tire ballasting, and 4% for miscellaneous uses including

refrigeration and in the shipping industry for freeze-proofing the bulk fragmentary shipment. Other minor uses include dehumidification, for addition in the manufacture of cement to decrease the alkali content of the clinker, for a weed control and soil compaction, as a brine medium in skating rinks, in the manufactuare of ice and preparation of frozen confections, in fireproofing the leaves of plants, and in drying of walnuts. Because of its high density (a 40°Bé* solution is one-third heavier than water), it is used as a ballast for tractor tires. As an industrial chemical, it is used in the recovery of certain metals from their ores and in the manufacture of algin** from sea weeds.

Markets served by calcium chloride industries in California are drilling well companies, concrete mixing companies, and timber harvest companies. Smaller markets served are dustproofing mines and roads, the refrigeration, and the ore dressing industries. California markets have not grown as fast as those of the rest of the United States because of mild winter weathers.

Total persons employed in the calcium chloride industries by various companies are about 25.

16. MINING METHODS AND BENEFICIATION

All the chemical companies working in Bristol and Cadiz Lakes employ three or more pumps to bring the brine out to the surface in the reservoir tanks or holding ponds. From the holding ponds, with the help of pumps, the brine is transferred to evaporation ponds or to long ditches (many miles long) for solar evaporation. Here, the temperature of the brine reaches 138°F in the summer months of July and August. Sodium chloride at this stage crystallizes (at 25°Bé) and sinks to the bottom. Calcium chloride liquid remains on top, where it is further concentrated up to 40°Bé. Then this liquid is pumped into the storage ponds and subsequently transported to users by trucks or by railroad tanks.

Hill Brothers Chemical Company's plant in Amboy buys liquid calcium chloride from Leslie Salt Company. They also haul some liquid calcium chloride from their operations in Cadiz Lake. From their storage tanks at the plant in Amboy, the liquid is brought to the concentrator and heated to 270°F. Then the concentrated liquid is passed to the crystallizers, where it is heated to 340°-350°F. After this, it is passed through the rollers

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* Baumé (Bé) is an arbitrary scale of specific gravities devised by the French chemist Antoine Baumé and used in the graduation of hydrometers. The relations to specific gravity (at 60/60°F) are as follows:
°Bé = 145 -[145/sp.gr.] (for liquids heavier than water); and
°Bé = [140/sp.gr.]-130 (for liquids lighter than water).

** Algin is any hydrophilic (having strong affinity for water), colloidal substance found in or obtained from various sea weeds.

with the chilling effects to flake the calcium chloride. After flaking, the product goes to the turbo driers, where calcium chloride is completely dried up and becomes anhydrous. This is then crushed up to the needed sizes, packed in plastic-lined, air-tight bags, and marketed.

17. CALIFORNIA EVENTS, TRENDS AND ISSUES

Future production and consumption of calcium choride are likely to increase rapidly because of the possibilities of development of new uses. The estimated reserves of calcium chloride in Bristol and Cadiz Lakes are enormous--perhaps enough to last hundreds of years. California has additional sources of calcium chloride in the geothermal brines of the Salton Sea area and in the oil field brines.

There are no environmental or reclamation problems involved in the process of mining calcium chloride from the brines because there is no residue waste dump left from this operation.

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